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# A study of the formation of gels of hydrated zirconia

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A STUDY OF THE FORMATION OF GELS  
OF  
HYDRATED ZIRCONIA

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A STUDY OF THE FORMATION OF GELS  
OF HYDRATED ZIRCONIA

A thesis presented to the Department of Chemistry  
of Union College in partial fulfillment of the require-  
ments of the degree of Bachelor of Science in Chemistry.

Walter A. Fallow

Approved by Charles B. Hurd

June 1940



## A STUDY OF THE FORMATION OF GELS OF HYDRATED ZIRCONIA

### Introduction

As silica gels and titania gels have been prepared and studied, it seemed logical that this investigation could be extended to zirconia gels. It has been the purpose of this research to determine the conditions necessary for the formation of zirconia gels and to initiate the investigation of their characteristics.

### Historical

A consideration of zirconia gels might well be prefaced by a summary of the chemistry of the zirconium compounds encountered in this work. Foremost among these are the hydroxide and the oxychloride. A complete review can be found in Venable's (15) monogram or in Meller's (8) treatise.

In the most general sense, the hydroxide is considered to be a hydrated dioxide. When ammonia, or an alkali hydroxide, is added to a solution of a zirconyl salt, a white, voluminous, gelatinous precipitate is obtained. If this is done in the cold, the precipitate is regarded as  $\text{Zr}(\text{OH})_4$  (ortho). When precipitation occurs from a hot solution the compound is assumed to be  $\text{ZrO}(\text{OH})_2$  (meta). The ortho dissolves readily in acid. The meta dissolves slowly although eventually to the same degree as the ortho. (The hydroxide used in this work is probably the meta.) The hydroxides are practically insoluble in water, sparingly soluble in concentrated alkali, and insoluble in solutions of alkali carbonates. In solution and accelerated by heating, the ortho hy-



droxide is thought to form the meta hydroxide.

Actually many more hydrated compounds have been postulated. VanBemmelen (14) found the fresh precipitate corresponds to  $\text{ZrO}_2 \cdot 127\text{H}_2\text{O}$  which upon drying in the air gives  $\text{ZrO}_2 \cdot 6\text{H}_2\text{O}$ . He concluded that the hydroxide behaves as a gel up to  $140^\circ\text{C}$  because the proportion of water varies continuously with temperature and vapor pressure of the water vapor. Between  $140^\circ$  and  $200^\circ$ , the proportion of  $\text{H}_2\text{O}$  is constant corresponding to the meta hydroxide. Above this, further dehydration occurs.

The hydroxide is amphoteric. Zirconyl salts are formed with strong acids and salts of the acid,  $\text{H}_2\text{ZrO}_3$ , are precipitated by strong bases although the actual existence of this meta acid has not been confirmed.

The zirconates are water-insoluble and are decomposed by acids.

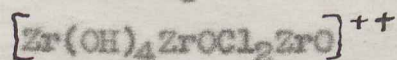
Zirconium oxychloride, the compound used in this investigation of zirconia gels, is a typical salt. It is formed by dissolving the hydroxide in dilute hydrochloric acid but is only slightly soluble in concentrated hydrochloric acid. The hydrate containing eight molecules of water is the normal hydrate. However many more basic hydrates are reported in the literature.

Pauli (9) has investigated the hydrolysis of zirconium oxychloride and has interpreted the results from the point of view of the hydro gel. (This report influenced the preparation of the standard solution used in this experimental



work). He concluded that simple hydrolysis in  $\text{ZrOCl}_2$  solutions is negligible. Freshly prepared solutions undergo continuous hydrolysis for three days at room temperature after which they remain unchanged for at least six months. Hydrolysis proceeds to 35 to 50%, with the solution remaining perfectly clear, and does not increase materially with dilution. Curves showing  $\text{H}^+$  and  $\text{Cl}^-$  concentrations vs. the concentration of  $\text{ZrOCl}_2$  are S-shaped and intersect at three points. At very low and again at moderate concentrations, the  $\text{H}^+$  is greater than the  $\text{Cl}^-$  indicating the presence of complex anions containing the zirconium. The fraction of the total chloride existing as free  $\text{Cl}^-$  varies irregularly with the concentration. As the conclusions are drawn from conductance measurements a large part of the conductance must be due to zirconium complexes which vary irregularly with the concentration of  $\text{ZrOCl}_2$ . The following bivalent complexes are typical of those assumed:

Cations



Anions



When the  $\text{H}^+$  concentration exceeds the  $\text{Cl}^-$ , more zirconium exists in the anion form and vice versa.

Pauli's (9) paper also included an investigation of  $\text{ZrO}_2$  sols made by dialysis of the oxychloride. Determin-



ations of the  $H^+$  and  $Cl^-$  were made at different concentrations. The  $Cl^-$  always exceeds the  $H^+$  but as the dilution increases, the two values approach each other with the fraction of the total  $Cl^-$  existing as free  $Cl^-$  decreasing with increasing dilution. The conductance is such that zirconium complex cations and anions must exist together although the cations are in excess. It is assumed that their numbers become more nearly equal upon dilution or prolonged dialysis and that coagulation results when the positive and negative complexes are equal.

Venable (17) investigated the hydrolysis of zirconium oxychloride and concluded that after three or four hours, the change in conductance was so slow as to amount to equilibrium. This collaborates work by Ruer (15) in 1902.

In 1902, Biltz (1) reported the formation of zirconium hydrogels from the nitrate, the oxychloride and the acetate. This is the earliest reference to actual gel formation that could be found.

Ruer (12) investigated the dialysis of zirconyl chloride. A hydro sol was obtained which retained some chloring that could not be precipitated by silver nitrate. Further dialysis leads to formation of a hydrogel. The protected chlorine was precipitated after boiling with nitric acid.

Prakash, (11) in India, has made zirconia gels in the course of his general investigation of gels. He reports obtaining the gels by addition of NaOAc only to  $Zr(NO_3)_4$  solutions. The addition of  $SO_4$  ions favors the formation



of the gel but the addition of  $\text{NH}_3$  was not necessary. This statement refers to his method of preparing gels of the hydrated oxides of the metals in which he assumes the following mechanism. A colloidal hydroxide, which is stabilized by the adsorption of metallic and hydrogen ions, is formed by the action of  $\text{NaOAc}$  on the metal salt. The function of the  $\text{NH}_3$  is to reduce the hydrogen ion concentration and to make the system liable to coagulation by  $(\text{NH}_4)_2\text{SO}_4$ . The latter gradually reduces the charge of the colloidal particles and the system becomes viscous, hydrates and gels.

Prakash reports clear, hard, transparent gels in the acid region with  $\text{ZrOCl}_2$  and sulpho salicylic acid and by the dialysis of a mixture of zirconium nitrate and potassium molybdate. (10)

In general, the method used by Jacober (6) and Godfrey (4) for the preparation of titanium gels was adopted for this investigation of zirconium gels.

#### Apparatus

The experimental technique adopted called for the slow addition of sodium carbonate to the zirconium salt with constant stirring. All solutions were to be at constant temperature. The basic unit was a thermostated bath, controlled by a mercury-toluene regulator attached to a thyatron heater. Control was within  $\pm 1^\circ\text{C}$ . From the bath, water was pumped by a converted automobile oil pump, through the jacket of a burette containing the carbonate. From this jacket, the



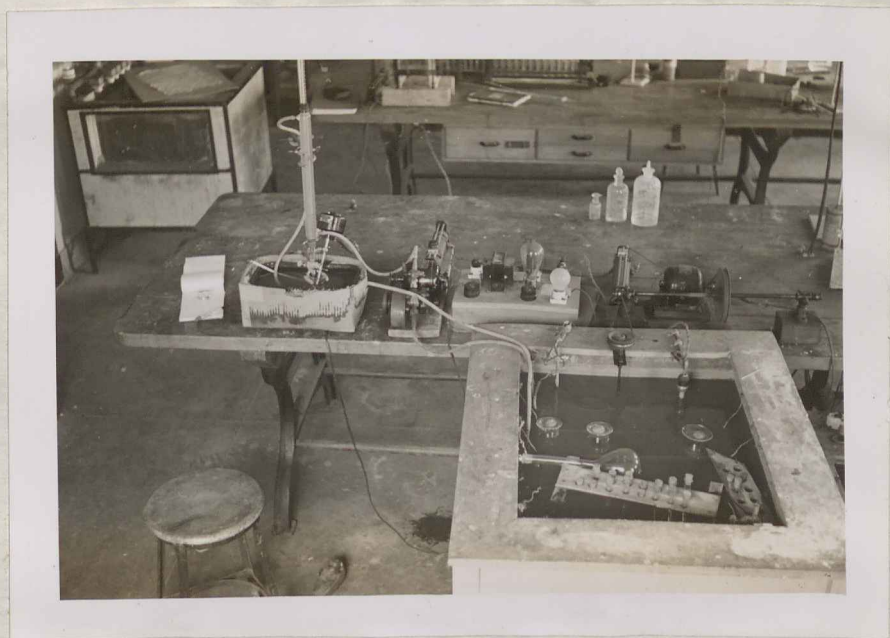


Figure 1

water was conducted to a secondary bath, which thermostated the zirconium solution during stirring, and back to the primary thermostat. Working at 25°C with the room temperature about 23°C, the secondary thermostat could be kept about .1°C below the primary bath. At 0°C and at 25°C, the error was about .4°C.

The stirring was done by a 7 mm. glass rod operated from a Cenco stirring motor and controlled by a foot switch.

### Experimental

Naturally, the first problem was to obtain a soluble zirconium salt standard from which to make the gels. An attempt was made to obtain a zirconate by fusion of the dioxide in a nickel crucible by methods outlined by Venable and Clark.(16) This proved to be impractical.

The oxychloride, hydroxide, sulphate and sodium salts of zirconium were obtained from the Titanium Alloy Manufacturing Company, Niagara Falls, New York. Only the oxychloride proved to be sufficiently soluble for the work. (The analysis of  $ZrOCl_2$ :  $ZrO_2$ -40%; Cl-22%; Fe-.05%; Ti-.05%). The hydroxide dissolved in acid, as previously mentioned, to give the zirconyl salt of the acid. No solvent was found for the sodium zirconate. Thus further efforts were concentrated on the oxychloride.

It was assumed that the hydrolysis of this compound reached equilibrium as discussed above and that such a solution would constitute a suitable standard. The first gels



obtained were formed by the slow addition of sodium carbonate to the oxychloride. However, the hydroxide, or the zirconate, formed (Martignac (8) says both precipitate together) as the carbonate was added was insoluble and redissolved in the acid medium only after long stirring. The same precipitation occurred with the alkali hydroxides, the alkali earth hydroxides and ammonium hydroxide. However, it was observed that the precipitate redissolved more rapidly when a dilute base was added slowly. Thus, investigations were conducted to obtain the best method of addition of base. Attempts were made to spray the base into the salt. This could not be done quantitatively. Solutions of sodium carbonate of varying concentration were added from a burette. To redissolve the fine precipitate formed in three minutes with a motor stirrer, the base could be no more concentrated than two tenths normal. However, with such a weak base, the volume required led to dilutions at which the gel was too weak and too long in setting.

It was considered desirable to add carbonate directly to the oxychloride solution to make a standard nearer the gelation point. It must be remembered that addition of the carbonate increases the pH rapidly while the simultaneous hydrolysis of the salt reduces the pH slowly. The solid carbonate must be added at a rate comparable to this hydrolysis in order to keep the pH below that of gelation. If this is not done, the mixture solidifies into a gel-precipitate mass which must be discarded. A solution was prepared con-



taining 385 grs of zirconium oxychloride (1.25 molar in  $ZrO_2$ ) and 80.26 grs of sodium carbonate per liter. The ph of this mixture remained at 1.85 for a period of sixteen days and was considered standard. However, a reading thirty-nine days later gave 1.74 as the ph. This standard was used in an attempt to determine the energy of activation. However, reproducible gels could not be obtained as the time of set increased daily. The results of work done at different temperatures on consecutive days had to be discarded as unreliable and a more thorough investigation of the factors affecting the time of set undertaken.

A new standard containing 385 grs of zirconium oxychloride per liter and 75 grs of sodium carbonate was prepared at a ph of 1.19. Only two temperatures were used in determining the energy of activation and all work was completed on the same day. The effect of stirring on time of set was considered. The mixture contained 25 cc of the standard and 40 cc of a .200 normal sodium carbonate solution. Time of set was recorded by the "tilted red" method. (5)



<u>Temperature</u>	<u>Stirring</u>	<u>Time of set</u>
34.6°C	2 min.	20:15
	3 min.	17:00
		18:20
		18:00
		17:45
	6 min.	16:30
25°C		16:45
	2 min.	91:00
		85:00
	3 min.	86:00
	4 min.	78:15
		81:00
	6 min.	78:15
		77:45
	8 min.	79:15

The ph for all these samples remained relatively constant and averaged 2.68.

These data are plotted in figure 2. The scale is chosen to bring out the percent change caused by stirring.

From these values, the energy of activation can be calculated using the relation

$$d \ln k / dt = E / RT^2$$

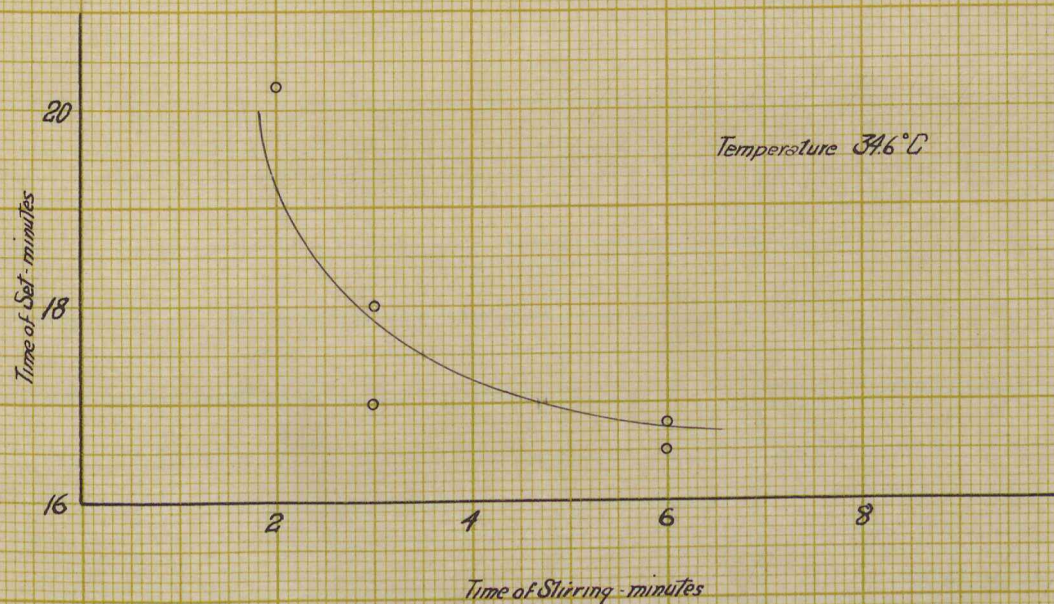
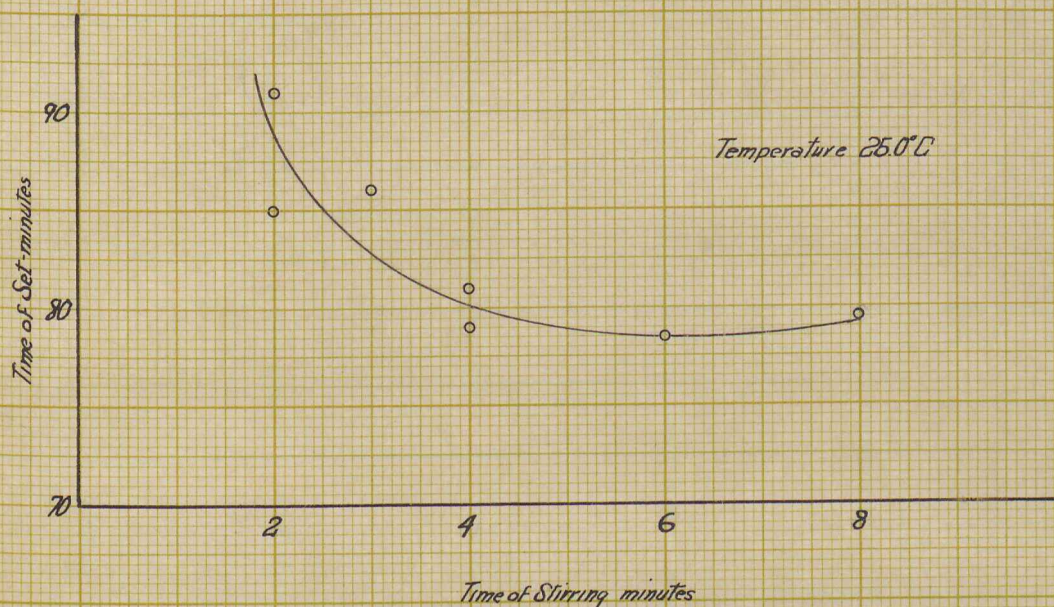
where time of set is taken proportional to k, giving

$$E = 2.3(R) \log t_2 - \log t_1$$

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$$1/T_2 - 1/T_1$$





Time of Set vs Time of Stirring

Figure 2



## Energy of Activation

<u>Stirring in minutes</u>	<u>cal/gr. mol.-degree</u>
2	28,820
3	29,220
4	29,170
6	29,430

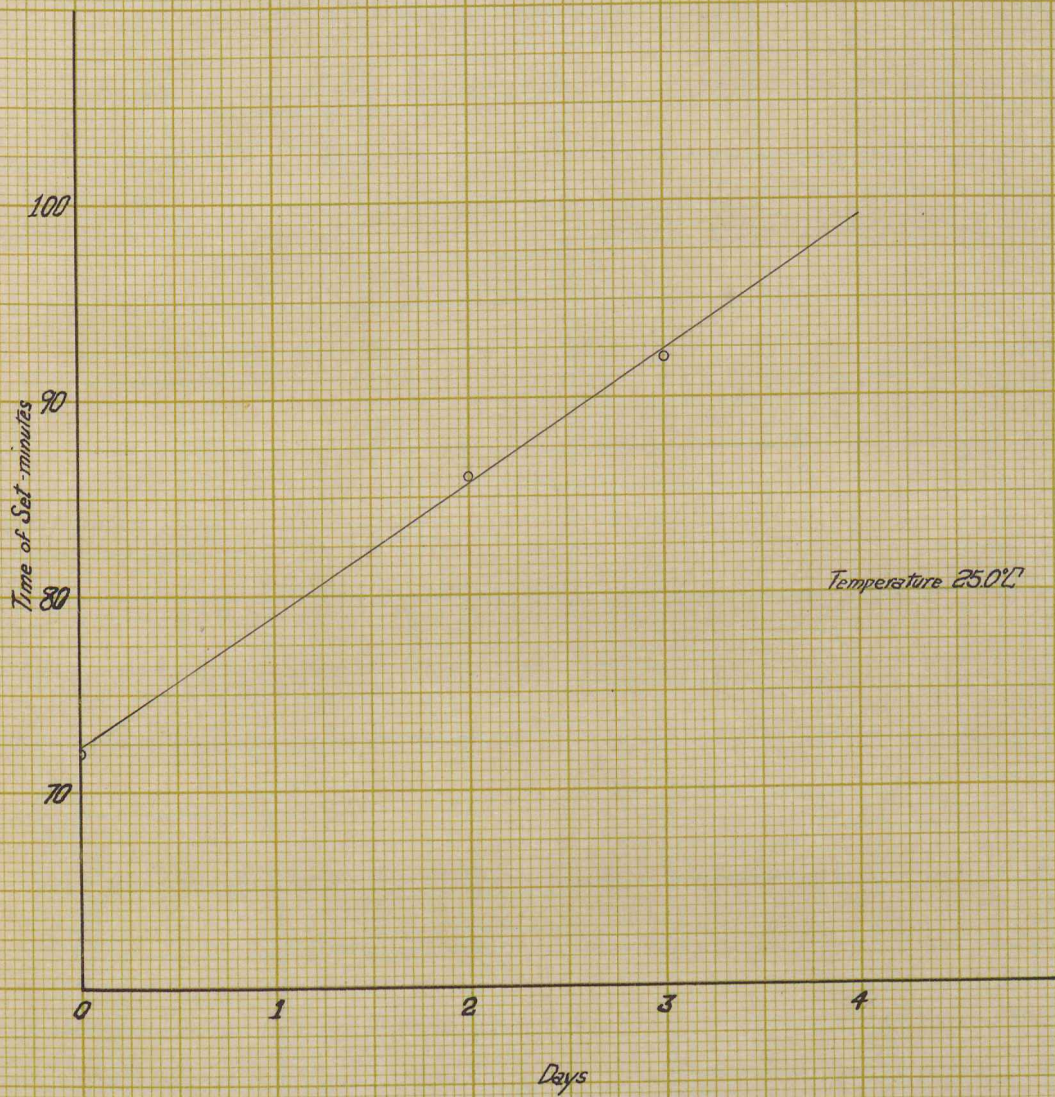
The daily variation in time of set is shown in figure 3. This is included to emphasize the necessity of making readings on a single day and to indicate the impossibility of undertaking a long study of the effect of a single factor on the time of set of zirconia gels made by this method. The composition of the gel is indicated above. Stirring was three minutes for all samples.

## Temperature 25°C

<u>Time of set in minutes</u>	<u>Time in days</u>
70	0
84	2
92	3

As these gels set, a surface crust seems to develop. This may be the result of capillary evaporation at the surface. As Esigmondy (7) explains, the vapor pressure is a function of the capillary meniscus radius. Thus it would be reasonable to assume that this radius may be large for zirconia gels and the vapor pressure relatively large. It should be noted that gels setting in corked test tubes did not appear to develop





Daily Variation in Time of Set

Figure 3



as strong a surface film. Perhaps this surface results from non-uniformity within the gel. In this connection the gel mixture, as described above, was allowed to set in an eight inch test tube and the specific gravity of the gel determined at the top (not including the surface) and at the bottom. The value of the former, 1.13; the latter, 1.20.

As this surface crust made the tilted rod method rather difficult, Flemming's (2) test tube method was tried. For this work, it seemed best to use dry test tubes filled with a funnel (to avoid wetting the tube and to give a sharp meniscus) to such a height that the weight of the liquid is supported by the gel structure alone excluding the possibility of support by a surface film. A height of three inches in a six inch test tube was considered satisfactory. An average value of 31,950 cal/gr. mol-degree for the energy of activation was obtained by this method.

As mentioned in the literature, zirconium hydroxide dissolves in hydrochloric acid to give zirconium oxychloride. It seemed reasonable to assume that gels from such a solution would be similar to those from the oxychloride solution directly. After five days, 125 grs of the zirconium hydroxide dissolved in a liter of solution containing 100 ccs of concentrated hydrochloric acid. The solution was yellowish-green and identical in appearance with a solution of the oxychloride. A standard was made up by addition of 54.25 gr/l of sodium carbonate to the above solution. The



following samples were prepared using 25 cc of this standard with three minute stirring. All were clear immediately after stirring.

	<u>Carbonate added-cc</u>	<u>Ph</u>
I	23	3.19
II	21	2.81
III	19.8	2.89
IV	19.3	2.80
V	19.0	2.74
VI	18.5	2.76
VII	18.0	2.58
VIII	16.0	2.52
IX	15.5	2.42

The general phenomenon observed was the appearance of an opalescence followed by a slow setting, of those with the higher ph, to a white, opaque gel with poor structure exhibiting synerses. The structure of these gels did not warrant a determination of energy of activation. Number one set within twenty-four hours. The others set at intervals. After two weeks number seven had set but would not hold a stirring rod. Number eight was opalescent but had not set and number nine remained clear. The contrast between these and the oxychloride gels will be discussed further in the following section.

While taking ph readings with the saturated potassium chloride electrode, it was observed that the gel became opal-



escent and set more quickly in the region adjacent to the electrode. This phenomenon was investigated further using 25 ccs of the above true oxychloride standard and varying amounts of saturated potassium chloride. Forty cubic centimeters of .200 normal sodium were added with three minute stirring.

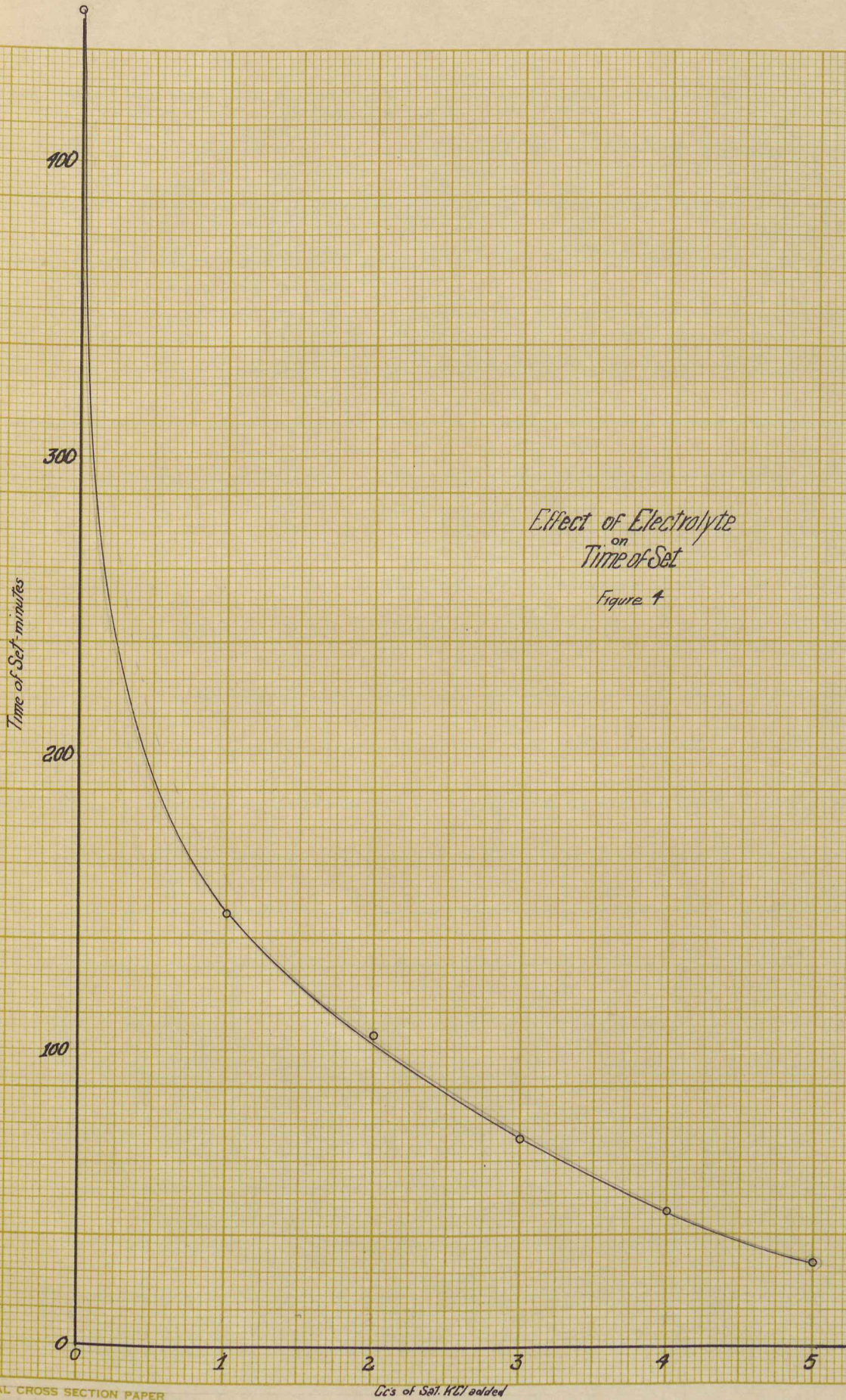
Temperature 25°C

	<u>H<sub>2</sub>O added-cc</u>	<u>KCl added-cc</u>	<u>Ph</u>	<u>Time of set minutes</u>	<u>Log of time</u>
1	5	0	2.72	450	2.653
2	4	1	2.68	146	2.164
3	3	2	2.72	105	2.022
4	2	3	2.89	70	1.845
5	1	4	2.86	46	1.663
6	0	5	2.89	28	1.447

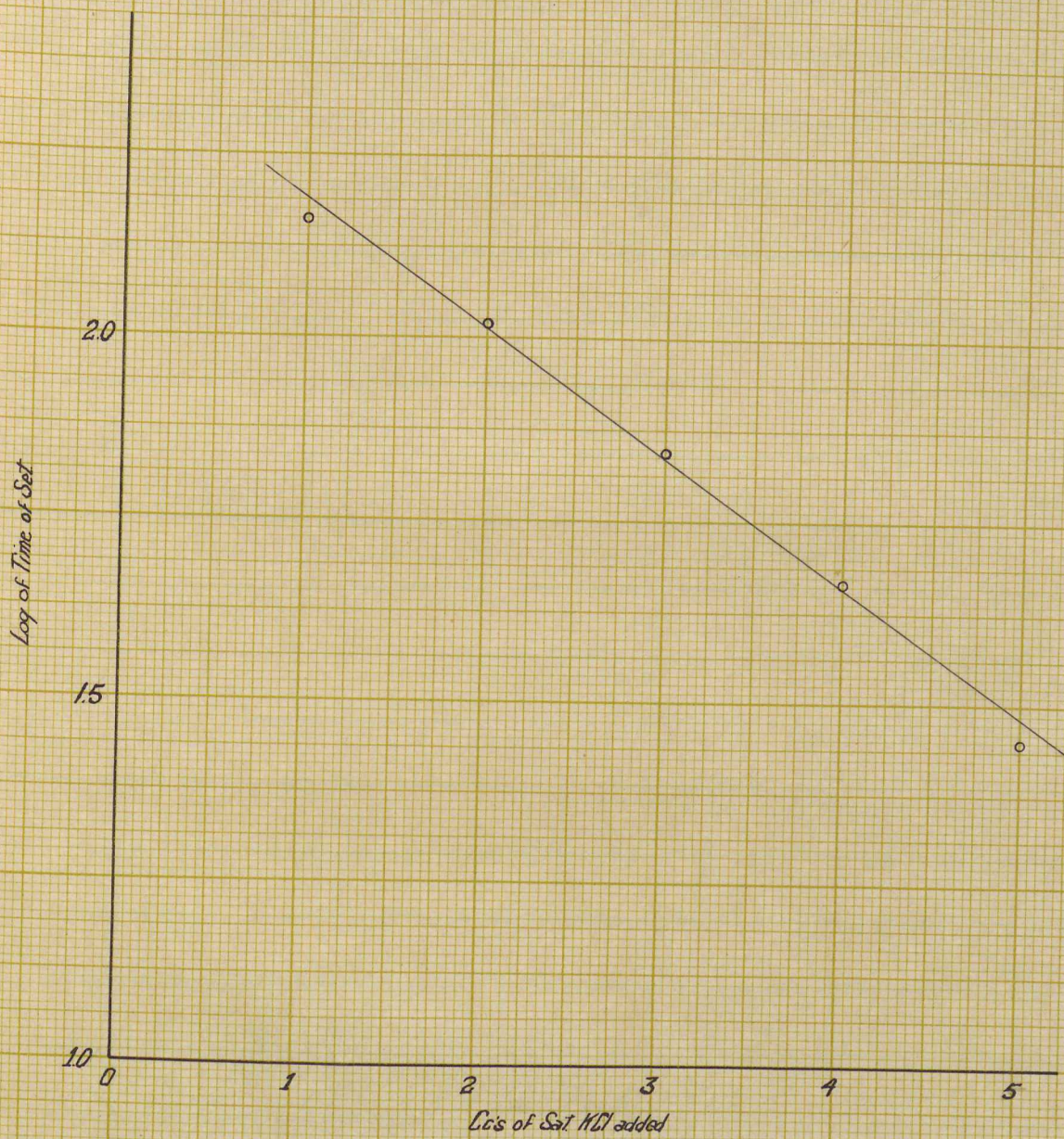
These data are shown in figures 4 and 5. The significance of plotting log of time against quantity of potassium chloride to show the phenomena of coagulation as presented by Freundlich, will be considered in the next section.

The question of heat reversible gels as presented by Godfrey (4) was considered briefly. The results did not show a clear confirmation. Any zirconia gel heated to about 90°C in a closed bottle will melt. The clear solution of one sample remained five months in this condition without change. A gel with time of set of about one hundred minutes at 25°C will set at 80°C before stirring can be completed. A gel









Effect of Electrolyte

Figure 5



having a reasonable time of set at  $80^{\circ}\text{C}$  will not gel if mixed at this temperature and cooled to  $25^{\circ}\text{C}$ . Such a sample, after standing a week at  $25^{\circ}\text{C}$ , gelled at about  $60^{\circ}\text{C}$  when heated slowly and finally melted, as described above, at about  $90^{\circ}\text{C}$ . The resulting solution could not be changed. This phenomenon does not seem to be one of heat reversibility. Rather, it seems consistent with the preparation of a standard solution which itself contains carbonate. Thus a standard for use at lower temperatures may safely contain more carbonate. This same standard may not be desirable for work in a higher range. The region above  $90^{\circ}\text{C}$  could not be investigated satisfactorily with this thermostatic arrangement. However, it appeared that a gel mixed within this region would set and then melt instead of remaining merely a solution.

### Conclusions

1. The daily change in the time of set and the resulting impossibility of undertaking extensive study of individual factors in relation to time of set of zirconia gels made by this method was demonstrated. This would appear contrary to the hydrolysis conclusions of Pauli based on conductance. Perhaps the equilibrium measured is limited to one of conductance and not necessarily to one of formation of complex ions. Strangely enough, the standard itself showed no signs of setting.

2. The energy of activation was determined as 29,200 cal/gr mol-degree at a pH of 2.68. This value is consistent



with 21,000 reported by Godfrey (4) and 16,600 reported for silica. In fact, these values plotted against the atomic weights of the elements give a reasonably straight line although it is hard to consider this significant in view of the complex ions postulated in gel formation. This value for zirconia does not fall on the curve plotted by Godfrey with titania and silica for energy against the ph.

3. Gels made from zirconium hydroxide were found to be of poor structure. In this respect, they appear to be similar to those of hydrated titanium dioxide as reported by Jacober.

It might be of interest to contrast the gels of zirconium oxychloride with those of the hydroxide in acid solution, remembering that those of the oxychloride are clear or slightly opalescent while those of the hydroxide are opaque. Prakash (10) considers that in the gelation, the particles exhibit two tendencies; one of hydration and one of agglomeration. If hydration is predominate the gel will be clear. If agglomeration is predominate the gel will be opalescent or opaque and of weak structure depending of course upon the degree of simultaneous hydration. No hydration during agglomeration results in coagulation and precipitation. This theory agrees well with the results obtained with the zirconia gels. Consider that in the hydrolysis of the oxychloride many seats of hydration are open as the chloride is removed



and complex molecules build up easily. As the charge is reduced by carbonate (the electrolyte), the hydrated molecules form the clear gel structure. In the case of the hydroxide, relatively few hydroxide groups are replaced by chloride as the hydroxide goes into solution. Pictorially, there are few seats of hydration open and large complex hydrated molecules do not form. When charges are neutralized, agglomeration is predominate. Thus in a broad sense, the solution and hydrolysis of the oxychloride, and the formation of an oxychloride in solution from the hydroxide and the mineral acid do not lead to the same products, as is generally reported in the literature. The oxychloride yields complex hydrated ions. The hydroxide yields relatively simple ions.

4. The reduction of the time of set by an added electrolyte was substantiated. This is in agreement with work done by Schalek (13) on ferric oxide sols. In his work, he found that these sols, when electrolyte was added, solidified to a gel which could be liquified by shaking. The time required for re-set after shaking was characteristic. By plotting the log of time of re-set against the concentration of electrolyte, he obtained a straight line and the following relation:

$$-k_1 \ln Z = C$$

Substitution of the velocity constant,  $x$ , which is inversely proportional to the solidifying time, leads to the equation:



$$-x = k_2 e c / k_1$$

On the basis of the results with ferric oxide sols, Schalek concluded that the uncommonly great electrolytic sensitivity of the solidification time as well as its quantitative characteristic indicates that this solidification must be a process identical with that of slow coagulation. The empirical formula may be regarded as an approximation to the theoretical formula for slow coagulation of Freundlich (3) and is sufficiently exact when limited to a moderate interval. Freundlich considers the velocity constant to be proportional to the number of active particles.

From the similar effect of electrolyte upon the time of set of zirconium oxychloride gels, it would seem reasonable to conclude that the gelation process involves the slow coagulation of highly hydrated oxychloride complex ions.



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